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BY

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The Growth of Etch-Figures

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INTRODUCTORY.

The extensive and ever growing literature which contains the results of investigators who have made use of the method of etching in order to obtain a more exact knowledge of various phases of crystal symmetry, is an evidence of the importance of this series of phenomena as a means of crystallographic research. Among these publications there have appeared from time to time papers which have been devoted to the study of etch-figures themselves rather than to their secondary application. It is evident from a study of these articles that many of the processes involved in the origin and growth of etchfigures have not yet been fully explained, and as these processes are intimately connected with the molecular structure of crystalline matter, the value of fuller information will readily be conceded.

A leader in the group of investigators who have devoted themselves to this phase of the subject is Professor V. Goldschmidt of Heidelberg, who published some years ago, two papers, among others, embodying a new theory for the formation of etch-figures.[1] According to this, both pits and etch-hills are the result of movements developed in the solvent. The chemical action between the corrosive and the substance upon which it is acting, gives rise to currents, some of which are directed towards and some away from the surface which is being etched. The interference of ascending with descending currents tends to form eddies, each of which is the starting point of a pit. The tendency of any solvent would be to produce regular, hemispherical excavations, but this is offset by the force of crystallization, which constantly endeavours to keep the corroded surfaces bounded by crystal planes. The resultant of these opposing tendencies is the typical etch-pit, whose sides are neither wholly irregular, nor yet normal crystal faces, but, as a compromise, planes of similar nature to vicinal faces. When a beginning has been made, the growth of the pit proceeds at a diminishing rate, and since the edges of the pit dissolve with greater rapidity than the walls, the natural result will be an increasingly indistinct outline and walls,

[1] Zeitsch. für Kryst., 38:273, 656. 1904.

which finally become practically indistinguishable from the surface of the crystal face. Then, newly developed eddies may form a fresh lot of pits in the enlarged bottoms of the old ones, and so the growth goes on.

At first sight the explanation of the phenomena of etching offered by this theory seemed to be quite adequate, but some facts which came to light in the course of an investigation made by the writer, of the symmetry of diopside seemed to point so clearly to a cause which lies much closer to the molecular structure of crystalline matter, that the present research was undertaken in order to attain to a fuller knowledge of these interesting and somewhat obscure phenomena. To this end it was necessary to devise special methods of investigation. In the first place, in order to observe the origin and subsequent stages in the growth of the pit, and to compare the rapidity of the action on the various faces of the crystal, it was exposed to successive, short applications of a corrosive in somewhat dilute form. In the second place, in order to trace these stages with greater certainty, the corroded crystal was examined at each step by means of the goniometer, and in the third place in order to study the distribution of the pits a series of parallel cleavage plates was etched. By these methods, the various stages in the growth of an etch-figure could be traced from a shapeless, shallow depression, through the next stage of the greatest perfection, with almost flat figure-faces which approximate true crystal planes, and finally, to the gradually disintegrating pit, whose sides become shallower and rounder until the whole disappears.

In order to observe these stages of growth various monoclinic minerals were etched. Colemanite, spodumene and diopside, on account of their transparency, their perfect cleavage and the ease with which satisfactory pits could be produced, were found to be the most suitable. The material was supplied by the Mineralogical Laboratory of the University of Toronto, where most of the experiments were carried out under the supervision of Professor T. L. Walker.

PART I—EXPERIMENTAL.

1. CORROSION OF COLEMANITE.

In several ways colemanite was found to be particularly well adapted to these experiments. It is obtainable in clear and transparent crystals and it has a perfect cleavage parallel to the clinopinacoid. It is thus possible to prepare plates so thin that the effects of corrosion on opposite sides can readily be observed and compared, and whose broad faces are

those which exhibit the maximum cohesion. Experience has shown that the most perfect examples of pits are produced upon such faces. This has already been observed by Baumhauer, who presents the facts in the following words: "Am besten entstehen die einzelnen Aetzeindrucke auf solchen Flächen, welche nicht allzu leicht vom Aetzmittel angegriffen werden, welche demselben also einen verhältnissmässig grossen Wiederstand entgegensetzen. Dies ist haüfig der Fall bei Spaltungsflächen"[2]. This necessarily follows from the fact that the phenomena of etching as well as those of cleavage are dependent upon the cohesion of the crystal.

It is a well-known fact that strikingly different results are obtained by the use of various corrosives, and so it is important to choose with care that one which is to be employed. In these experiments with colemanite three acids, each in a very dilute form, were successively tried, namely citric, acetic and hydrochloric.

Citric acid produced etch hills. In cases where the solution was very dilute and the action had been early discontinued, the surface of the cleavage plate was covered with closely lying hills of polygonal form, fitted together like tiles in a pavement. As the process progressed, certain of the hills became undercut leaving an overhanging part somewhat resembling the beaked extensions of pits to be subsequently described. Frequently these projections, all pointing in the same direction, had the appearance of being oriented.

As a result of many experiments to determine the effect of the corrosive in various degrees of dilution, it was found that with extremely dilute acetic or hydrochloric acid, the pits were very small, and that with corrosives of greater strength the pits became larger. A 0.5% solution of glacial acetic acid acting on the clinopinacoid, produced great numbers of four-sided pits so small that it required the highest available power of the microscope to observe their details. Along with these well-defined pits there were also shallow depressions with indefinite outline. Some of these had a deeper part which approached somewhat tc the form of a pit. An interesting feature was the occurrence in almost every clear pit, of a beak-shaped extension, sometimes many times longer than the pit itself, growing from the deepest part of the figure. As solutions of greater strength were used, the percentage of beaked pits grew steadily less, and the beaks became shorter, until, when the optimum strength was reached, they were practically absent.

[2] "Die Resultate der Aetzmethode in der krystallographischen Forschung." Leipzig, 1894, p. 3.

When a solution of double the strength was used, that is 1.0%, results were obtained which differed only in degree from those already described. The pits were larger, the beaks were shorter. The ill-defined figures mentioned in the previous paragraph were not observed, but each pit was surrounded by a shallow depression in which it seemed to have been developed (Plate XXVI, fig. 1). A curious feature noted here was that the beaks of two adjoining pits had become united, forming a connecting tube (Plate XXVI, fig. 2). It was noted also that the pits were not evenly distributed, the surface of the crystal being in some places closely covered, and in others comparatively free. The significance of this phenomenon, which has been frequently referred to by previous investigators, and which will be more thoroughly discussed on a later page, forms the basis of one of the main deductions of this paper.

Stronger solutions gave larger, clearer pits and still shorter beaks. When 2% had been reached the pits were still very minute, and those on one side appeared to differ from those on the other in their rhombic outline, being more nearly lozenge-shaped. Distorted pits, enclosed by four non-parallel sides, two of which were distinctly longer than the others, were frequently seen.

In consequence of the fact that, with colemanite, hydrochloric acid acts much less vigorously than acetic acid, the action of the former was more readily controlled and the results were correspondingly more satisfactory. It was found that a 1% solution gave pits which were much more primitive than those in the experiment previously described, in which a solution of acetic acid of half the strength was used, and there was the advantage that the pits were somewhat larger. Under these conditions there were produced numerous small, shallow depressions, whose sloping sides lacked the definiteness of figure faces. In most cases the depth was greater in one part, and set within was a clearly defined pit. (Plate XXVI, fig. 3). We shall see that a similar primitive form was met with in the investigation of the figures on diopside.

At this point, use was made of the method of exposing the crystal to the intermittent action of the same corrosive. After the first exposure to a 2% solution the surface was found to be covered with shallow, lozenge-shaped, asymmetric pits, set close together in parallel arrangement (Plate XXVI, fig. 4). There were no beaks. The pits observed after a second exposure had steeper sides (Plate XXVI, fig. 5). Some of these may have been the result of further development of the previous forms, but a few at least were new figures growing upon the sloping sides of the earlier ones. While further action resulted in the dissolving away of the etched surface in most cases, it was observed that here

and there the old centres of action remained and the pits grew downwards into the substance of the crystal (Plate I, fig. 6). Alongside of these there occurred great numbers of minute pits of a new generation and a new quadrilateral form somewhat like the typical pits on the clinopinacoid of diopside to be described in a subsequent section (Plate I, fig. 7). Some of these, it should be remarked, had rudimentary beaks. Subsequent action did little more than slightly increase the size of the pits already formed, and after the seventh test it was finally discontinued.

Since Baumhauer, in the article already referred to in these pages, had spoken of the occurrence of beaked pits, a phenomenon not observed in these tests in which dilute hydrochloric acid was the corrosive, a new series of experiments was designed to determine whether they could be obtained by using solutions of greater concentration. Three solutions were accordingly prepared containing respectively 4, 6 and 8% of the acid, and each was allowed to act upon a cleavage fragment. In the first case the comparatively large, four sided pits produced, although their general outline was typical for the clinopinacoid, were lacking in the full symmetry in having their deepest part asymmetrically located (Plate XXVI, fig. 8). When the strength of the solution was increased to 6%, still larger and clearer pits were produced, some of which had fine, hair-like beaks (Plate XXVI, fig. 9). In an 8% solution very clear, straight sided pits were formed but stronger solutions resulted in pits of less distinctness. Evidently a corrosive of medium strength is the most likely one to produce beaked pits.

From time to time pits had been observed which were characterized by minute extensions somewhat resembling beaks, but growing out from one of the angles of the pit and not from the bottom. When a 10% solution was used this phenomenon was strikingly evident. On a careful examination, the projection was seen to consist of a narrow crack running downwards from the surface of the crystal face in such a way as to appear like an extension of one of the side faces of the figure. Similar pit formations as observed in other crystals will be referred to in a subsequent section of this paper.

One group of these experiments was designed to throw some light upon the problems of the point of origin of the pit. It will be remembered that Professor Goldschmidt had suggested that each pit indicates the place where currents have started in the corrosive, and that the growth of the pit is the result of the continuance of these currents. It was observed however that characteristic corrosion was obtained in the foregoing experiments, even when the test tube was vigorously shaken. Further, remembering that in the process of electro-metallurgy, similar

currents are avoided by keeping the solution in constant motion, the effect was tried of directing a small jet of the corrosive against the crystal and then quickly stopping the action by plunging it below the surface of water. Under these conditions no ascending current of sufficient force to overcome the jet which was being directed against the crystal could have been formed, and yet clearly defined pits, though small ones, were produced.

It becomes quite evident that we must look for some other explanation for the origin of pits. When we examine an etched crystal we cannot help noticing that the pits are not scattered evenly over the surface, but that some parts are comparatively free and some densely covered. This fact had already been observed by Baumhauer,[3] who remarks: "Die Vertheilung der Aetzfiguren über die geätzte Fläche ist nie eine gleichmässige, wie man nach der Theorie erwarten sollte".

Tentative explanations for this irregularity have from time to time been brought forward, and as this problem includes the fundamental one of accounting for the origin of the individual pit, it was necessary to devise experiments to put the various theories to practical tests. Several fragments which had been marked with fine scratches were etched, but instead of the etch-figures being more numerous over the scratches, the latter were at once smoothed away by the corrosive. It had been suggested that possibly small particles of dust might provide the corrosive with points of attack, and that the fortuitous scattering of the dust particles might reveal itself in the apparently unaccountable distribution of the pits. In order to test this several pieces which had been covered with dust were exposed, but in no case was there any increase in the number of pits, or any concentration on that part of the surface where a greater amount of dust had collected.

Another possible explanation for this bunching of the pits was that the crystal might have been under strain, but a careful microscopic examination of several very thin slices from crystals which had shown this concentration of pits, failed to give the irregular extinction under crossed nicols, which is to be expected in strained crystals. This is of course what one might have expected, since pitting is a function of the cohesion of a crystal and strain is the result of abnormal elasticity.

Among the crystals used in these experiments some were transparent while others were translucent. The transparent crystals, in some cases at least, produced large and clear pits, which were not set very closely together, while the surface of the milky crystals was closely covered with small, indistinct pits, making the crystal still less transparent.

[3] op. cit., p. 6.

This milkiness was found to be due to the presence of numerous small inclusions. There would thus appear to be some connection between the number of pits and the number of inclusions, and it seemed quite possible that the uncovered top of an inclusion might form a ready point of attack of the corrosive. But, while in a given experiment the pits are of approximately the same size, the inclusions on the other hand vary, some being many times the size of the largest pit. Further, it was found that the places where most pits were produced were not the areas of the greatest distribution of the inclusions, and finally, in no case was an inclusion seen to be the starting point of a pit. We may safely conclude then that the relation between inclusions and pits is not that of cause and effect, but rather that of a common origin. The ability of a growing crystal to take up impurities from the surrounding solution, and the frequency of the occurrence of possible points of attack for the corrosive on the faces of a mature crystal, alike depend upon abnormalities in its cohesion.

An observation of Baumhauer's in his paper on the apparently anomalous pits of colemanite, when more fully worked out, gave a clue to the elucidation of this problem. He found that if the two cleaved halves of a crystal which have been subjected to the action of a corrosive, be placed together in their original position, pits on the two halves will be found to coincide and thus form a negative crystal, which is divided, sometimes in the centre, but more frequently unequally, by the plane of cleavage. The bearing of this phenomenon upon the problem of the origin and cause of pitting, was not discussed or suggested by this investigator.[4]

Following this experiment, a piece of the mineral was cleaved into halves, which were then etched separately, but under similar conditions. It was found that the size, number and distribution of the pits on adjacent sides of the plane of cleavage were quite similar, and even in some cases complementary pits could be identified. But the distribution of pits on opposite sides of the same fragment was always different, and sometimes a difference was also observed in their size and development and even in their shape.

A suggestive fact which came to light in this experiment was that the negative crystal which would be formed by bringing the two pits on adjacent faces together, was not divided symmetrically by the cleavage plane. The deepest part of one pit will then be found opposite the shallowest part of the other. In fact the two pits are enantiomorphous

[4] Zeitsch. für Kryst., 30: 97. 1889.

(Plate XXVII, fig. 36). It would appear that this fact has a bearing upon the grade of symmetry of the crystal.

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2. ACID CORROSION OF SPODUMENE.

In order to obtain etch-figures upon the prismatic faces of spodumene, a small cleaved fragment was exposed to the action of concentrated sulphuric acid and fluorite over a low bunsen flame. After an exposure of five minutes no result was visible, but when the same fragment had been subjected to an additional exposure under the same conditions for ten minutes longer, numerous, clearly defined pits were observable. Of these primitive pits three types were noted which were bounded by three, four and five sides respectively. The triangular form appeared to be the youngest.

These typical primitive pits were each bounded by one short, straight side and two larger, curved ones (Plate XXVI, fig. 10). The angle *B A C*, which contained the deepest part of the pit, was read in one sharply defined example as 80° 48′. These pits were shallow and gave no indications of figure faces, but were simply slight depressions deepening towards one corner. Along with them were others which, judging from their depth and distinctness, were somewhat more mature. In them the sides had increased in number to four, and were no longer curved but straight. Instead of being mere shallow depressions, these pits were enclosed by four definite figure-faces, two being unequal scalene triangles and two unequal deltoids (Plate XXVI, fig. 11), but even yet the structure was somewhat lacking in clearness. It will be noticed that they could be produced from the pits of the first type by truncating the angle *B A C* by the line *D E*. In addition to these two forms, there were a few which at first appeared to belong to another group characterized by a five-sided outline (Plate XXVI, fig. 12). These may, however, be considered as derived from the four-sided pits by a further replacement of the angle *B C A* by the line *G F*. None were observed of a shape which would suggest the replacement of the angle *A B C*. It will be seen then that the three main types of pits produced upon the cleavage face of spodumene may be looked upon as variants of the same primitive type, and further, as representing three stages of growth through which the individual pit would pass if conditions were favourable.

Along with these occurred some examples of a fourth type which had a more distinctive appearance, owing to the occurrence of beaks. This has been supposed by some investigators to have a bearing upon the question of the grade of symmetry shown by the crystals of this mineral and others, especially diopside and colemanite. They are

illustrated in Plate XXVI, fig. 13. It will be remembered that in the most primitive type one corner, that near the point A, was always deeper than the rest of the pit. In some instances this deepening was very pronounced, occasionally even being prolonged into a knob (Plate XXVI, fig. 14). The beak, whenever present, extended from this corner. Finally in some instances pits had been formed which appeared to be composed solely of the beak enormously developed. To so great an extent had this occurred in a few cases, that a tube had been produced which apparently ran along parallel with the surface, and emerged again at a considerable distance in another small pit. This resembles what we saw in the etching of colemanite, in which small pits were joined by a connecting tube, but in the latter case they were larger and more clearly defined.

It will be seen that the pits thus developed on the cleavage face of spodumene are of considerable diversity. All of these however may be considered, from the circumstances under which they were produced, to be comparatively young, and in order to have examples of a more mature type, another fragment of the crystal was exposed to similar corrosion conditions for a period of thirty minutes. After this somewhat lengthy exposure there was found a series of pits of various stages of development. While some of them gave evidence of a greater maturity there were still others which resembled that previously described as apparently the most primitive type. This suggested the idea, which further experiments showed to be the correct one, that as corrosion continues not only are the existing pits deepened and matured, but new and immature ones are constantly coming into existence.

The most distinct of these forms consisted of a shallow, triangular depression, differing from that observed in the specimen etched for fifteen minutes in being bounded by straight lines (Plate XXVI, fig. 15). The outlines seemed to be those of a right-angled triangle, but on measurement the angle $A\ B\ C$ proved to be 96°, while the angle $B\ A\ C$ was 53° 27′. Other less definite examples of this form gave values for the more obtuse angle of 105° 24′ and 112° 7′ respectively. This may be looked upon as a modification of the form first described, but differing from it in its deepest and best developed part lying between the sides $B\ A$ and $B\ C$. Some of the figures, by their size and distinctness indicated a still greater maturity. Not only were they very much deeper, but two of the three sides appeared to cut perpendicularly, while a third sloped gradually (Plate XXVI, fig. 16). In fact, in some of the examples the steeper sides seemed actually to overhang. This formation of an overhanging edge, a peculiarity which will be referred to later, is a rather unexpected phenomenon. Goldschmidt draws our attention to

the fact that the action of solution will take place with the maximum of rapidity on any edge, more particularly if that edge is at all acute, and in this way the pits become flatter as action continues. But here are examples of the persistence of a well defined and sharp edge.

Along with the forms described above there were others which from their distinctness of outline and depth would appear to be somewhat more mature still. They were bounded by three unequal, triangular figure faces of which the largest was curved. An additional peculiarity was that which has been referred to in the previous paragraph: the deepest part was not in the centre of the pit but was very much to one side, being in fact under an overhanging edge. In all the pits of this type, the figure-faces appeared to be striated parallel with the surface of the etched face. The significance of the phenomena just described will be dealt with in a subsequent part of this paper.

Pits of a still more mature form were obtained by exposing the specimen to the corrosive action of the commercial solution of hydrofluoric acid. After ten minutes' heating over a water bath the corrosive had produced, not the forms which we usually think of when we speak of pits, but fine tubes. The openings to these tubes were larger than the tubes themselves and to a certain degree resembled true pits. On continued action they increased in a remarkable manner, not only in number, but also in length, becoming twisted and interwoven like a bunch of hairs. The growth of these tubes continued with further exposure to the corrosive long after the surface originally acted upon had been completely dissolved away. After an exposure of fifty minutes when the action was discontinued, some of the tubes seemed to have penetrated nearly half through the fragment. This rather extraordinary result seems to have a bearing upon the nature of schillerization as will be seen from the discussion in the second part of this paper.

In the experiment described above, in addition to the corrosion which produced the fine tubes in the interior of the crystal, another and different type was observable on the surface. Gradually the pits which were first formed enlarged their borders until by the coalescence of numerous flat bottomed pits the whole surface with the exception of a few residuary etch-hills had been removed. On these freshly formed surfaces new etch-figures began to appear. While they were still of a somewhat triangular form, being composed of three figure-faces, one long and shallow, a second slightly shorter and steeper and a third small, steep and triangular, yet they showed considerable variation from the first crop produced upon the unetched face. After an exposure of thirty minutes they were fairly large, of clear general outlines but the form of the figure-faces was not easily seen. After forty minutes

they had become not only more numerous but also more clearly defined, and by fifty minutes they were quite mature and distinct. This series of reactions is of interest when considered in connection with the experiments above described, in which adjacent sides of cleavage fragments were simultaneously etched. It would appear that the distribution of pits is determined by the molecular conditions of the crystal face, and that after the whole layer has been removed by corrosion, a new layer with new possible centres for pitting, is brought to light. The significance of these facts is more fully discussed in the second part of this paper.

Two slight irregularities in the form and arrangement of the pits remain to be noted. Greim, in describing the somewhat similar figures on diopside, remarked that the position of the positive and negative hemi-pyramids could be determined by the direction of the triangular pits.[5] Now in the specimen examined, although the acute angle of most of the pits on any given prismatic face would, as a rule, point in the same direction, yet there were fairly numerous examples whose orientation was just the opposite. Again, it was frequently noted that opposite faces in the crystal were acted upon by the corrosive in quite a different manner. One side for instance gave a predominance of the normal triangular pits, with a few of the beaked variety, while the other was characterized by the presence of only a few ordinary pits, and those of a much greater size, the rest being mainly of the beaked type. There was also no apparent connection between the number and arrangement of the pits on opposite sides. On one side, the pits might be very abundant and uniformly distributed, while those on the other would be restricted to one or two small groups. The colemanite experiments of the previous section go a long way towards explaining this apparent anomaly which has been frequently commented upon.

The occurrence of pits of different types on the same crystal face has been noted by many investigators, and suggests several interesting problems, some of which will be referred to later when dealing with the pits obtained by the corrosion of diopside. In the case under consideration at least, it would appear that the various forms are not to be looked upon as differing in kind, but merely in their stage of development.

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3. Alkaline Corrosion of Spodumene.

The production of pits upon spodumene by alkaline corrosion is not so readily achieved as by the use of hydrofluoric acid. The corrosive

[5] Jahrb. Min. u. Geol., 1889, I: 252.

acts with very much greater rapidity, and the specimen frequently becomes covered by a layer of an insoluble silicate which cannot be removed. Several corrosives were used, first a fused mixture of sodium and potassium carbonates, which proved to be altogether too vigorous, then a solution of sodium carbonate at 100° C., which after a very long exposure resulted in a few small and doubtful pits. Finally sodium hydrate was tried, and after an exposure of two minutes over a bunsen flame, pits were obtained of moderate distinctness. When the operation had been interrupted at one minute no pits were found, and after seven minutes' exposure the specimen had been almost dissolved away.

The pits produced differ distinctly from those obtained by acid corrosion. The alkaline pit on the cleavage prism is typically asymmetric and bounded by five sides (Plate XXVI, fig. 18). It has five figure-faces of unequal size and different shape. The angles in some of them were as follows:

ABC	123° 48′
BAC	56° 18′
BCD	90° 0′

It is interesting to note, however, that here as in the case of the prevously described acid pits, the values of the angles were found to vary quite considerably, in one case the angle *B C D* was seen to be 108° 18′.

The tendency observed in the case of acid etching, for the replacement of corners by additional figure-faces, was quite noticeable here also, for pits were seen which had six sides (Plate XXVI, fig. 19). On account of the difficulty in obtaining pits at all, it was not found possible to observe the stages in their growth, but judging from analogy to the results obtained from acid pits on spodumene, as well as to those to be described, obtained from diopside, it would appear that these extra faces were added as the pits attained greater maturity. This process appeared to be more pronounced in alkaline etching, with a resulting tendency to a more complex outline.

A similar example of the occurrence of a larger number of faces in alkaline than in acid pits was found in some etched material kindly placed at my disposal by Professor Walker. Among other preparations of the micas, there were some of phlogopite etched by hydrofluoric acid and fused caustic potash respectively. In the former, most of the pits were of a simple triangular outline while in the latter they were mainly six-sided with the appearance of the face of the hexoctahedron.

On one of the etched faces of spodumene, each one of the pits was provided with a funnel-shaped beak somewhat similar to that obtained

under special circumstances in acid etching. Here, as in the previous experiments, the numbers of the pits on the opposite sides of a crystal were not the same.

In comparing these pits with those described for acid corrosion, no clear relationship was observable. These are typically quadrilateral and those triangular, but there is one shallow, five-sided form illustrated which could apparently have been derived from a triangular form by that replacement which this paper shows to be so characteristic of the growth of etch figures (Plate XXVI, fig. 20).

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5. ACID CORROSION OF DIOPSIDE.

The excellence of the material procurable made it possible to carry out the corrosion experiments with greater thoroughness in the case of diopside than with spodumene. The faces of the prismatic zone of the former were readily obtained in brilliant condition, and the base and clinopinacoid which are invariably rough and unsuited for crystallographic investigation were artificially cut and polished on one specimen. It was thus possible to prepare a more complete series of the pits of diopside than had yet been published so far as the writer has been able to discover. It was found that not only did the pinacoids give better pits than the prisms, which were the only faces available in the spodumenes, but that the various stages in their development were more clearly defined.

(*a*) *Pits on the prisms.*

A crystal of transparent diopside from De Kalb, N.Y., was exposed to the corrosive action of a mixture of powdered fluorite and sulphuric acid heated over a low bunsen flame for two minutes. On the prisms small pits of a very primitive form were developed (Plate XXVI, fig. 21). They were mere shallow depressions bounded by two sides, one straight and the other curved. One angle was slightly more obtuse than the other, and at this point was situated the deepest part of the pit. In some cases which appeared to be rather more mature, the figure was a steadily deepening groove, one end of which had become a dark, indistinctly bordered hollow.

On continued exposure to the corrosive an interesting modification of the primitive pit was observed. Gradually the borders of the indistinct deep portion took on a definite appearance, until after four minutes there had been developed a quadrilateral pit, bounded by four unequal, triangular figure-faces (Plate XXVI, fig. 22), lying at the end of the shallow depression which represented the primitive pit. As the corrosion con-

tinued, the quadrilateral pit became less clearly defined and finally assumed the form of a shallow depression, in some cases suggesting the more primitive first stage.

Under similar conditions pits of the same type were produced upon the prism faces of other examples not only from the same locality, but also from Zillerthal. In one case, however, while the pits on one side were like those already described, the adjacent prism exhibited pits of a new form. They were of an unusually deep, almost square shape, composed of four triangular figure-faces meeting at an eccentric point.

Experiments of a similar nature had already been made by Greim.[6] In his description reference is made to two types of pit, enclosed, one by three, the other by four, triangular figure-faces. It would seem probable from the preceding experiments, that the two types of Greim are merely pits in two of the stages of that development which is characterized by a successive interpolation of additional figure-faces, as has been brought to light by the method of intermittent etching.

(*b*) *Pits on the clinopinacoid.*

Pelikan[7] experimenting with Nordmark diopsides etched by hydrofluoric acid, produced pits on the clinopinacoid which he described as of two kinds as follows:

(1) Shallow, of rhomboidal outline, the longer pair of sides being parallel with the prism edge, the other pair inclined in the direction of the edge between 010 and 001. Frequently the sharp angles are truncated by a pair of small faces making the pit six-sided.

It will be noted that such a pit would represent the grade of symmetry to be expected on the clinopinacoid of a monoclinic crystal, a face possessed of a binary axis of symmetry. His second type, which did not indicate a symmetry of so high a grade, was described as:

(2) Apparently deeper than (1), usually of somewhat rhomboidal outline, but with the upper edge parallel to the edge between the basal and clinopinacoids.

This is a pit without an axis of symmetry.

These two forms sometimes occurred in correlated position such as might be expected upon the face of a crystal twinned parallel to the orthopinacoid, but as they were not found in vertical rows, Pelikan concluded that this position was not the result of twinning but of a difference in the molecular structure of the crystal. This peculiarity would seem to be inherent in the diopside molecule, for he found these two types in all diopsides examined, and in augites of a chemical com-

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[6] op. cit.

[7] Min. u. petr. Mitth., 16: 1. 1896.

position approximating that of diopside, while in true augites the pits were quite normal. This would indicate a grade of symmetry lower than that usually conceded to diopside.

In a critical examination of these results Baumhauer[8] quoted his own previous investigations of Ala diopsides etched by a hot mixture of fluorite and sulphuric acid. In these experiments he had produced pits of the following four types:

(1) Microscopical unevennesses on the unetched faces;

(2) Long, rounded pits, frequently united to form furrows, approximately normal to the edge between the orthopinacoid and clinopinacoid;

(3) Rhomboidal figures, inclined obliquely towards each edge;

(4) Deeper, six-sided forms apparently the result of a greater development of (*c*).

All of these would indicate the presence of a binary axis, the condition of monoclinic holohedrism.

He next examined one of Pelikan's etched crystals on which he found only two definite types of pits:

(1) Deep, dark, holohedral monoclinic pits whose longest side is rotated slightly to the left of the edge between the clinopinacoid and the prism;

(2) Rhomboidal, symmetrical, shallow pits.

His examination of the specimen led him to believe that the other forms described by Pelikan were either very immature pits which if allowed to develop under more corrosion would become symmetrical, or were the result of the fusion of the two general types. In this way he discounted the conclusions of Pelikan as to the symmetry of diopside.

The investigations of Greim which had been published nearly ten years earlier, did not altogether agree with those of these crystallographers. On the clinopinacoid of his crystal from Alexander, N.C., etched by dilute hydrofluoric acid, he had found two types of pits, one bounded by four figure-faces, two parallel trapeziums and two triangles. The other was enclosed by five figure-faces, two pairs of parallel trapeziums and a rhombus. The latter was parallel to the clinopinacoid and its sides were parallel to the upper edge of the figure and thus it formed the bottom of the pit.

This very great divergence between the results of careful experimenters, working with crystals of the same kind, under conditions practically identical, seems to be due to their comparison of pits of different ages. In none of these cases was anything said as to the length of time the corrosion had continued, and by noting the progress of the

[8] op. cit.

action from time to time, as described in the previous section we arrive at the conclusion that age is an essential factor in determining the form of the pit. This became more evident by the following experiments which were made with a view to the determination of the changes which take place during the growth of the pits on the clinopinacoid.

One of the first points to be noted in the experiments to this end is the striking difference between the rates of corrosion on the various faces. The crystal first used, when corroded sufficiently to give clear pits upon the prism, showed an orthopinacoid almost entirely removed, being covered with a closely lying series of long parallel grooves. A similarly striking difference between the rates of corrosion on different crystals was also observed, for, when a crystal of spodumene and one of diopside were heated together in a mixture of fluorite and sulphuric acid over a low bunsen flame for thirty minutes, on the cleavage plane of the former there were well-defined pits while each face of the latter had been etched into hills.

After a sixteen-minute exposure to the action of fluorite and sulphuric acid over a bunsen flame good pits were obtained upon the clinopinacoid. Many of them had a regular rhomboidal form, being enclosed by four triangular figure-faces (Plate XXVI, fig. 24). In some cases however the parallelism of the sides was not perfect, with a result that the symmetry of the pit was of a lower grade than was to be expected on the clinopinacoid of a monoclinic crystal (Plate XXVI, fig. 25). A few even showed the replacement of one of the angles by a fifth face (Plate XXVI, fig. 26).

On a specimen from Zillerthal etched for $33\frac{1}{2}$ minutes by dilute hydrofluoric acid at 100°, some interesting pits were obtained whose orientation indicated the occurrence of repeated twinning. The position of the several individuals of the twin was shown by pits lying side by side in reversed position (Plate XXVI, fig. 27). Between these were pits which were bilaterally symmetrical showing the position of a plane of symmetry. These evidently lay over the edge of the twinning face. Apparently the point of origin of the pit was on this edge, resulting in a kind of pseudosymmetry.

In the experiments here described, pits were obtained which correspond with all those mentioned in the papers to which reference has been made. Most of them are of Pelikan's first type which is about the same as the third of Baumhauer, and the first of Greim. A number were like the second of Pelikan in which the two shorter sides are not parallel. Several of the experiments resulted in pits in which the absence of parallelism was characteristic of the long faces and in some cases neither pair was parallel. The additional pair of figure-faces mentioned by Pelikan was frequently observed, but did not seem always to charac-

terize the asymmetric pit, but in several cases one of the corners had been truncated, resulting in five-sided pits. In one case, a pit similar to the second type of Greim was observed (Plate XXVI, fig. 28). It is also important to note, in view of Baumhauer's explanation of Pelikan's supposedly asymmetric pit, as being the result of twinning, that in the case above mentioned, where the twinning was apparent, the result was not to lower the grade of symmetry of the pit, but actually to raise it.

(*c*) *Pits on the orthopinacoid.*

It has already been pointed out that the orthopinacoid is attacked with much greater rapidity by acid corrosion than is the prism or the clinopinacoid. An exposure of three quarters of a minute to a heated mixture of fluorite and sulphuric acid resulted in the entire solution of the face. Another specimen exposed for a quarter of a minute only, had its orthopinacoid etched into a series of long, parallel grooves, which completely covered the face. Hydrofluoric acid at 100° was next used and a specimen exposed for one quarter of a minute still showed an over-etched orthopinacoid. So, for subsequent experiments it was diluted with an equal amount of water and was found satisfactory.

After an exposure under these conditions, of six and one-half minutes, the first clear pits were obtained. They were enclosed by six sides, the longest pair parallel with the vertical axis of the crystal, the other two pairs closing the ends of the pit, one of which was considerably more acute than the other. This represented a figure enclosed by twelve faces as shown in Plate XXVI, fig. 29.

It differs from the pit obtained by Pelikan on this face. He describes it[9] as a long deltoid, the sharp end of which points towards the base, the obtuse towards the orthodome. Similarly Hintze[10] speaks of the pit as a deltoid with rounded sides, the acute end directed towards the negative, the obtuse towards the positive pyramid. However it is similar to those illustrated by Daly[11] as obtained by etching diopside from Ala with hydrofluoric acid.

In order to obtain if possible a more definite knowledge of the faces which enclose the pits, the Goldschmidt reflection goniometer was used. This is the method already followed by the designer of the instrument in the investigations referred to above. The crystal was set up with the face whose pits were to be examined normal to the axis of the instrument, and the reflections from the pit faces read in the usual way. In view of the clearness of the pits which had been obtained, it was natural

[9] loc. cit.

[10] "Mineralogie", 2: 1020.

[11] Proc. Amer. Acad. Arts and Sci., 34: 430. 1889, pl. IV, 15.

to expect that these would be found to be enclosed by ordinary crystal faces, and that reflections from them would be clear and distinct. In this case it would be expected that the reflections would be thirteen in number, a central one representing the unetched crystal face; two on each side in a direction normal to the vertical axis of the crystal, representing the long faces and four on each side of a line connecting these, forming roughly, if joined, two crossing lines, representing the smaller faces.

Instead of this, the reflections took the form of a bright band, brightest in the centre, from which point it steadily became fainter, until at some distance at each side there was a break, followed by a hazy spot at the end. There also extended from the centre two fainter lines above and two below in a slanting direction. This figure would represent the reflections from a boat-shaped pit whose sides and bottom are alike curved. Subsequent investigation however tended to show that this curvature was only apparent and that the effect was due to the fact that the figure faces are numerous, small and differing but slightly in their inclination to the axes.

An additional exposure of the same crystal, bringing the total up to $9\frac{1}{2}$ minutes, under the same conditions, gave pits which were more distinct and considerably larger. When set up on the goniometer as before and examined, it was seen that while the reflection was, as in the previous experiment, in the form of hazy bands, the central one had become noticeably shorter, and all through it were scattered more or less distinct spots of light, which would indicate that for the first time some of the figure faces were large enough or flat enough to yield definite reflections. However they were rather numerous and close together, and consequently could not all of them represent possible crystal faces.

Further exposures gave results of steadily increasing clearness. After the total had been $13\frac{1}{2}$ minutes several of the reflections were the best so far observed. This improvement continued on additional application of the corrosive, until the total time was $23\frac{1}{2}$ minutes, after which there was no increase in the distinctness. Corrosion was discontinued in the case of this crystal after $33\frac{1}{2}$ minutes, but other crystals were etched under the same conditions for a very much longer time. A white diopside from Zillerthal in fifteen minutes, gave small and numerous pits on the orthopinacoid. After further action for fifteen minutes, the pits were sufficiently well developed to give clear reflections, but after a total of forty-five the point of greatest perfection had been passed and the larger, shallow pits were no longer definite enough to be read on the goniometer. Another specimen, a green diopside from

De Kalb, N.Y., reached its greatest clearness in about fifty minutes. These experiments indicate that a maximum of perfection, in which the figure-faces approach to the condition of possible crystal faces in their evenness and position, is attained only after etching has been continued for a considerable time. Further exposure results in gradually decreasing clearness, until the pits have quite lost their original character.

It is interesting to note in passing that in these experiments, as in others in this research, one or two of the pits attained a size many times greater than that of the rest on the same face, persisting even after others had flattened out of all resemblance to their original form. This fact is of significance in developing the theory of the origin of etch-figures as will be seen by the discussion in the second part of this paper.

(*d*) *Pits on the orthodome.*

The faces around the ends of the vertical axis of diopside are almost invariably extremely rough and corroded and quite unsuited for crystallographic examination. In order to overcome this difficulty some crystals were obtained which had the forms (101) and (001) artificially cut and polished upon them. Before being etched they were examined and the artificial faces were found to be correctly cut.

After an exposure of 20 minutes to very dilute hydrofluoric acid, quite definite but minute pits were obtained on the domes. In general form they were somewhat lozenge-shaped. They were each bounded by four figure-faces, two pairs of triangles, one of which was considerably longer than the other. In some cases, a fifth face, small and four sided, formed the bottom (Plate XXVI, fig. 30). It will be noted that this arrangement results in a figure, one of whose ends is deeper than the other. At this stage, the pits were too small to yield any definite reflections of any kind.

On further exposure to the same corrosive the pits gradually increased in size and number and to a certain degree changed in outline. A few were observed which were enclosed by two curved figure-faces. This stage of their development is shown in Plate XXVI, fig. 31.

After thirty minutes' exposure it was found that the pits were still too shallow to admit of measurements, and so a stronger corrosive, commercial hydrofluoric acid diluted with an equal volume of water, was used. This, after an exposure of 20 minutes at 100° gave pits which, while they retained their original outlines, were much larger and deeper. While the perfecting of the faces took place apparently in the same way as in the case of the pits on other faces, the action was not continued long enough to give any clear reflections.

In his experiments with the amphiboles, Daly[12] obtained well defined and uniform figures on the orthodome. They were usually of a regular triangular outline enclosed by three triangular faces. Occasionally however they were five-sided, the result of interpolation of pyramidal faces at the basal angles of the original pit.

(*e*) *Pits on the base.*

The conditions under which corrosion takes place on the basal pinacoid are quite similar to those under which it acts on the domes, and the resulting pits as will be seen from the drawing (Plate XXVI, fig. 32) are very similar, the only difference being that they are somewhat shorter. This shortening is suggestive when we compare the pits on the three principal faces in the ortho-diagonal zone, in which, beginning with the long, almost furrow-shaped figures on the pinacoid, the pits become shorter as we approach the base, where the length is at its minimum.

After an exposure of 20 minutes to a 50% solution of commercial hydrofluoric acid at 100°, conditions under which the figures were developed upon the domes, corrosion had so far progressed that the reflection showed, as in a previous case, a nebulous band in which were a few more or less distinct spots. Further corrosion did not increase the distinctness of the reflections, on the contrary they appeared to become more and more hazy.

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6. Alkaline Corrosion of Diopside.

In order to obtain pits by alkaline etching, specimens were exposed to the action of fused sodium hydrate, but unlike spodumene, diopside became rapidly over etched and covered by an opaque layer which no amount of washing or boiling with acids would remove. A solution of the same alkali proved ineffectual, but after an exposure of 15 seconds to fused calcium chloride, although the faces of the crystal frequently became clouded, minute but fairly clear and characteristic pits were produced upon the prisms. They were bounded by three sides, one short and straight, the others long and curved and approximately of the same length (Plate XXVI, fig. 33). They were enclosed by three triangular figure-faces, one of which had all three sides straight, while each of the others had one curved side, and were frequently arranged in vertical rows with their short sides lying parallel to a cleavage trace. The only indications of etching upon the pinacoids at this stage were slight roughenings.

[12] op. cit., page 413.

A thirty second exposure gave pits of somewhat similar form but with the two curved faces replaced by two short straight ones (Plate XXVI, fig. 34). This suggests that in alkaline etching the same series of events takes place as that which we have seen in the case of acid etching, namely the replacement of curved lines by several shorter straight ones. However, it was difficult to obtain clear pits and in consequence there was not sufficient data upon which to generalize. Extended corrosion, while it seemed to make the pits upon the prisms clearer, did not enable one to obtain any upon the pinacoids. After 40 seconds' exposure, there were no clearly defined pits upon the orthopinacoids, while the clinopinacoid had merely minute, ill-defined spots of roughening.

PART. II—THEORETICAL.

1. INTRODUCTORY.

In the first part of this paper there is described a series of experiments with three monoclinic minerals, together with a statement of the observed phenomena. It now remains to combine these results so as to see their bearing upon the general problem of the origin and growth of etch-figures, and as we do so the processes involved begin to take upon themselves a somewhat new significance.

The new generalizations to be deduced from the data now at our disposal may be stated briefly as follows. In the first place the point of origin and the distribution of the pits depend upon the molecular structure of the crystal and not upon any external and adventitious cause. In the second place in its development a pit passes through a regular series of stages comprising growth, maturity and decay. In the third place, there is a relationship between the faces of the pits developed on the various faces of a crystal, and in the fourth place the beaks are shown to be of three kinds, and suggestions to account for their occurrence have been offered.

2. THE POINT OF ORIGIN.

As has been pointed out in the experimental part of this paper, one of the striking and unexpected features of etch reactions is that the pits are not distributed evenly over the crystal. The question why one part of the etched face should be free from corrosion, while adjacent parts are closely covered with pits, is one which has attracted the attention of many investigators, and in consequence many explanations have been offered. It is evident that in order to provide an adequate theory

for the general distribution of pits it will be necessary to arrive at a knowledge of the conditions which cause the selection of one point for the location of a pit in preference to another.

Before formulating any new theory it is necessary to review briefly those already suggested and to point out in each case wherein it has failed to satisfy the test of experimental verification. It has been supposed that the presence of extraneous particles such as dust upon the surface would provide points of attack for the corrosive. The experiments in which dusty crystals were exposed without corresponding results, and also the fact that the irregularity is as striking on fresh cleavage faces, show that this idea is quite untenable. But it is possible that there may be fracturings or scratches on the surface in which the corrosive could find a lodgement, unhampered by currents, and so a start might be made. Direct experimental disproof has already been offered in the account of the colemanite experiments, and Daly[13] has shown that such surface fracturings cannot be the universal cause, for in the case of an alum crystal growing in a saturated solution of the salt, a slight dilution of the liquid results in the immediate formation of pits. Under these conditions the crystal faces must have been perfectly unbroken. His conclusion is that the arrangement is "structurally accidental". The possible connection between pits and inclusions which the experiments with colemanite seemed to indicate, was on further consideration seen to be one of a common cause and not of cause and effect. There remains now, in addition to Goldschmidt's theory as outlined in the opening pages of this paper, another, suggested by von Ebner[14], which supposes that the pit originates at the point where particles of the corrosive of greater concentration than the average come in contact with the crystal. Both of these theories are put to the test when action takes place in boiling solution and in a shaken test-tube, and also when the corrosive is applied in the form of a jet. Under such conditions there can be neither eddies nor differences of concentration in the solution.

Since all of these theories fail when put to experimental test, one must look for a clue leading to a new explanation of this unexpected state of affairs. We must bear in mind however, that whatever the conditions may be that allow a selective attack by the corrosive, they must be common to adjacent sides of each cleavage plane, since on these the arrangement of the pits is the same. A suggestive fact in this connection is the growth of pits in overlapping parallelism in more

[13] op. cit., page 389.

[14] Sitzber. d. Akad. d. Wissensch. zu Wien, 89: 368. 1884.

or less straight lines. Pits occurring in this linear arrangement were described by Baumhauer[15], who called them "Aetzgraben". These lines are usually irregular, but examples have been frequently observed in which definite crystallographic directions are thus marked by rows of pits. For instance, Böhmer described pits on quartz crystals of concentric growth, which were found to have a corresponding concentric arrangement parallel to the combination edge between $+R$ and $-R$.[16] An even more suggestive example was that previously referred to in the case of diopside, in which the pits were found along the edge of a twinning plane.

It is evident that these lines of selective pitting are also lines of weak cohesion, and we must remember that those faces which present the maximum cohesion, such as cleavage planes, are corroded much more slowly than those of a lower degree. It has also been noted[17] that when a crystal has been fused, the resulting amorphous substance has a lower specific gravity, indicating that the molecules are farther apart, and in consequence the cohesion must be less. Such material has less resistance to the attack of the solvent than had the original crystal. In other words, the stronger the cohesion the greater the resistance to corrosion.

It seems evident therefore that wherever cohesion is less than the average for any crystal face, there is in consequence a point where the corrosive can begin its action. In certain particular cases, such as along the edges of cleavage and twinning planes, the connection between the location of pits and points of weak cohesion is clearly seen, and in others, while not quite so evident at first sight, this relationship is demonstrable, for there can be nothing else in common which could account for the similarity of the arrangement on adjacent sides of cleavage plates. We are now in a position to deduce the law that the point of origin of every pit is at a centre of weak attachments between adjacent crystal molecules. Since, in the process of solution, fresh surfaces are constantly being formed, each of which has its own crop of pits, we conclude that all through the mass of the crystal there are scattered these points of potential pit origin.

It is interesting to note, however, that some individual pits have the capacity of attaining a much greater size than the rest. At first the pits are practically of the same dimensions, but as time goes on, here and there some will be found to be noticeably large. In the ex-

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[15] "Resultate", page 6.

[16] N. Jahrb. f. Min., Beil. Bd., 7: 540. 1891.

[17] Walker, "Crystallography", N.Y., 1914, page 44.

periments with colemanite it was noted that some of the pits grew vertically downward into the mass of the crystal. In the diopside experiments pits were observed on the orthopinacoid which developed to great size and perfection.

These differences cannot depend upon the corrosive, as they are formed under various conditions. They cannot be accidental in view of what we have already seen as to the causes of the first pit formation. It seems therefore reasonable to suppose that the centres of weak cohesion are more extensive in some cases than in others.

The theory of the distribution of centres of weak cohesion throughout the crystal gives us an explanation for another peculiarity of etching. Daly has observed[18] the occurrence of what he calls "stepped pits", which are deep forms whose sides have a laminated appearance. He explains these as being due to the edges of parallel cleavage planes being brought to light by the corrosion. Pits of this type, while few in number, have been observed from time to time in the course of this research, the most notable instance being that referred to and illustrated in the experiments with colemanite. If a centre of weak cohesion, and therefore, one of potential pitting, be of sufficient extent to lay bare, before the pit has reached its limit, another such centre, the result will be a pit within a pit, and this process, if carried still further, will result in a large pit of the stepped type. The steps in each case being the remnants of the bottoms of the pits which have been so enlarged.

Our deduction as to the point of origin leads us a step further. Since pits are not distributed evenly over the etched face, it follows that the centres of weak cohesion are similarly irregularly placed. Hence the cohesional attachments of a series of crystal molecules in the face will not be uniform. In consequence, the cohesion of any crystal face, as indicated, for instance by its hardness, is not an elementary quantity, but is the mean of an infinite number of variables.

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3. THE GROWTH OF THE PIT.

Von Ebner in his paper on the etch-reactions of calcite and dolomite concluded that some figures are instantaneous and. some retarded,[19] but Baumhauer remarks: "Instante und retardirte Aetzfiguren sind Endglieder Reihe von Formen, welche sich durch verschiedene Geschwindigkeit der Entwickelung unterscheiden. Sie sind durch Uebergange mit einander verbunden".[20] In the experiment above described

[18] op. cit., page 396.
[19] op. cit., page 775.
[20] "Resultate", page 4.

in which a current of somewhat concentrated corrosive was directed against a crystal of colemanite, the well-defined pits which were produced apparently instantaneously, differed only in size from those produced slowly by a more dilute solution.

The inference is that by the use of a strong corrosive the pits are produced more rapidly than with a weaker one. Many authorities have gone a step farther by the claim that such pits are also more perfect. Miers summarizes this as follows: "Experiments with hydrochloric acid on cylinders of calcite indicate that with a more concentrated solvent the etched faces are produced more readily and in greater perfection than with a dilute solvent".[21] The results of the foregoing experiments, however, show that approximate perfection in the figure-faces depends, not upon the strength of the solvent, but upon the completeness of the processes involved. With a weak solvent this will take place slowly, but in time the result will be the same.

That there is a development of some kind in the formation of the pit has long been known. It is referred to by Baumhauer,[22] who points out that the pits become more numerous and larger until the surface is practically covered. He also observed that after a time they become rounded, but the stages in this process have not hitherto been definitely laid down. It was also made note of by Daly, who remarks, "As the process of etching continues the pit usually increases in size, often (depending partly on the symmetry of the etched plane) changes in shape of outline. . . . The first stage of development in a pit may be called its 'initial' form. The development ends where the outline begins to be seriously impaired by the solution of the surrounding part of the etched surface. Just preceding this point in the history, the pit may be called 'mature', and the process intervening between the initial and mature stages is that of maturing. Von Ebner's 'instantaneous' and 'retarded' types are connected by transitions, but are not easily to be compared to 'initial' and 'mature' figures since his types refer simply to the length of time required to develop the pits and are not restricted to the use of one solvent".[23]

By the application of the method of interrupted etching, the existence of this development was proved and the various stages were isolated and described. They may be stated as follows:

(1) The first stage in pit development is ultra-microscopic, and consists of the attack of the corrosive upon the weak point in the crystal. From this, the rate of attack depends upon the strength of the corrosive.

[21] "Mineralogy", Lond. 1902, page 115.

[22] op. cit., page 3.

[23] op. cit., page 376.

(2) The second, or immature stage is characterized by a shallow, rounded excavation and outlines which are composed of few and curved lines.

(3) As corrosive action continues, the edges which bound the pit tend to become straighter and there is developed in one part a small but definite pit which grows larger, eventually almost filling the primitive depression, which now appears as a slight shadow. Just as the outlines of the primitive pit are curved, so also the earlier figure-faces appear to be curved, though this, as will be seen in the succeeding section, is due, at least in part, to the occurrence of numerous small faces of almost the same symbols, close to one another. During this process the faces become clearer and plainer, and the interpolation of new figure-faces of different indices and in different zones may take place resulting in pits of a more complex outline.

(4) There is a point of maximum perfection, beyond which continued corrosion results in less distinct faces and a broadening rather than a deepening of the pit.

(5) When the edges of expanding pits overlap, leaving a fresh surface marked by etch hills, renewed corrosion results in the formation of a new crop of pits.

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4. THE NATURE OF THE FIGURE-FACES.

The comparative regularity of the outlines of etch-figures and the apparent evenness of their planes, naturally suggest the idea that they are bounded by simple faces. This was the view of the earlier investigators, whose results were obtained by means of the microscope. Leydolt,[24] the first to consider the problem, thought it possible to express their relationships by means of simple symbols.

But with the application of more exact methods, there came a growing conviction that figure-faces are not as simple in their crystallographic relationships as was at first believed. An examination by Sohncke of the four-sided pits of common salt,[25] showed the symbols of their faces to be 910 and 10, 10. Still further discrepancies were observed by F. Klocke in alum pits[26] whose figure-faces had the symbols 778, 557, 15 1 15, 30 1 30, etc.

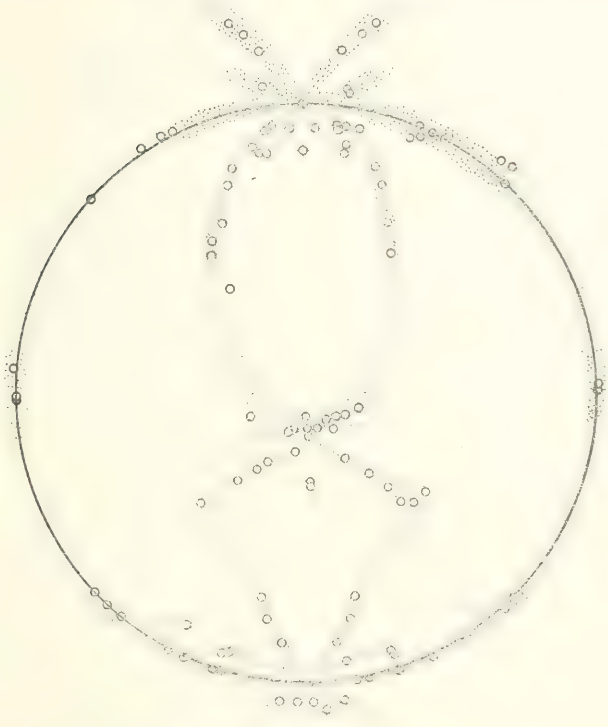
When Goldschmidt made use of his two-circle goniometer in the investigation of the subject, the anomalous nature of the pit faces be-

[24] Sitzb. der Akad. d. Wissensch. zu Wien, 6 Nov. 1854.

[25] Jahrb. f. Min. 1875, page 941.

[26] Zeitsch. f. Kryst., 2: 126.

came more strikingly evident. The reflections from figure-faces are then seen to differ in a marked manner from those which would be obtained from a series of normal crystal faces. They consist of a number



of light-paths radiating from a common centre. In some cases the rays are long and join in a small central patch of light, and in others it is the centre that is well-defined, and the light-paths are short and indistinct.

In order to make a careful study of these phenomena as exemplified by diopside, a crystal which had been exposed to a 50% solution of

hydrofluoric acid for 15 minutes was mounted on the goniometer and readings were made at intervals along each one of the light-paths Although they were frequently quite dim, they could still be traced in an unbroken series around the crystal in several directions, as is shown in the accompanying stereographic projection. This is characteristic of all the zones.

These observations show very clearly that the faces which form the sides of a pit, and which on microscopic examination resemble crystal faces so closely, are in reality very different. In no case do the parameters bear a simple ratio to one another. In fact, the only type of crystal face with which they seem to have anything in common is the vicinal face.

The length and the continuity of the light-paths would seem to indicate that the reflexions are those from curved faces, and this has been generally assumed. But there are two suggestive observations which militate against this assumption. In the first place, scattered among these indistinct rays there are to be found faint signals like those which might be expected from very small faces. Again it was frequently observed that in order to trace the light-paths it is necessary to move the crystal so that various parts of each face come successively into the field of vision. Further, it was also found that by narrowing the aperture of the telescope's eye piece, the light-paths become shortened and replaced by a series of hazy spots, and sometimes change into clear, though faint crosses.

Evidently then the continuity of the light-paths is not due to the curvature of the figure-faces, but to the fusion of reflexions from numerous pits. This leads to the rather unexpected deduction, which is, however, borne out by numerous observations, that the corresponding figure-faces of pits on the same crystal faces are not identical, though their difference is slight.

Although we must not look upon pits as being enclosed by true crystal faces, it is evident that their bounding planes represent as close an approximation as possible under the circumstances. Goldschmidt has pointed out that in pit formation there are two opposing tendencies, one of which would result in the formation of round excavations if unopposed, and the other in the development of true crystal faces. Thus the net result is these faces which are approximately regular, and hence are of value in the determination of the physical properties of crystals.

Since the symmetry of any pit is an expression of that of the crystal face upon which it is developed, it is natural to expect that there would be some relationship between the pits on various faces of the same

crystal, of such a nature that the form of any one could be predicted. This form is determined to a certain extent by the relative rates of solution in different crystallographic directions. Some pits are long and narrow on account of a marked difference in the rates of solution at right angles to one another, while others are square or even nearly round where there is no difference in the rates. This point has been worked out in some detail by Becke,[27] who, by careful measurements of the diameter of spheres during the process of corrosion, deduced the rule that the velocity of solution varies with the crystal direction. From these velocities it would be possible to construct an ellipsoid of solution corresponding to those illustrating the phenomena of heat and light in the crystal.

Another method of showing the relationship between the pits was suggested by the fact brought to light in the diopside experiments, described in an earlier section of this paper, that the pit on the base resembles that on the orthodome, while the latter resembles to an equal extent, the pit produced upon the orthopinacoid, the three differing mainly in their comparative lengths. In each pair there are some faces in common, and it would be possible to construct a negative crystal from the faces occurring in the pits of the orthodiagonal zone. The result would be substantially the same negative crystal which would be obtained by the union of two pits on opposite clinopinacoids. If it were possible for the corrosive to act within the mass of a crystal, just such a regular cavity would be the result, and, in passing, it might be pointed out that Professor Judd's remarks as to the cause of schillerization, which are quoted on a subsequent page of this paper, would indicate that such an action is not so impossible an event as might at first appear.

In order to discover experimentally whether we have in such a negative crystal a method of correlating the pits of a crystal, a plaster model was made consisting of the following forms: (100), (110), (010), (001), and (011). This is similar in shape to the cast obtained by filling the negative crystal formed by bringing together pits on adjacent clinopinacoids. The portion of the model cut off by any intersecting plane will then represent a cast of a similar portion of the original negative crystal. In order to obtain a cavity corresponding to that of the cut off part of the negative crystal, it is only necessary to imbed this in solidifying plaster in such a way as to keep the hypothetical plane of section in a horizontal position. This was done and the intaglio models so formed are illustrated in the accompanying plate.

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[27] Min. u. petr. Mitth., N.F., 5: 457.1883.

It must be borne in mind, however, that the figure-faces of the models are those which might be expected to be formed in etching if their development could go on unhindered. That is to say, the pits in the models are enclosed by the minimum number of simple, plane faces, not the indefinite and vicinal faces which we find in actual experience.

The model representing the pit on the orthopinacoid will be observed to be similar to that obtained by etching, with the exception of the faces which close the lower end. These are so inclined as to leave an overhanging edge. This, as has been pointed out by Goldschmidt, in the article already referred to, will provide a point of vigorous attack for the solvent, until the edge is entirely removed. Thus we have the typical pit on the orthopinacoid. It should be remembered in this connection, that in a specimen that has been somewhat overetched one end of each pit is much less clearly defined than the other. The whole pit appears as a groove closed at one end and gradually becoming shallower, until it reaches the surface of the crystal face. The reflection from an orthopinacoid covered with pits of this kind shows a bright light-path corresponding with the prismatic figure-faces, two moderately bright ones corresponding with the faces at the well-defined end, and some faint traces, representing the other end of the pit. This was repeatedly observed in examining crystals with etching developed to this extent. All of which shows that at the point where according to theory we should expect the maximum amount of corrosion, this special rounding off of the pit edges actually takes place.

The model representing the theoretical form of the pit on the orthodome, will be seen by comparing it with figure 31 of Plate XXVI, to bear a striking resemblance to the pit actually obtained by etching. Similarly we find the same relationship between the theoretical and experimental results in the case of the pit on the basal pinacoid, as shown by referring to Plate XXVI, figure 32. In both model and drawing, the faces closing the deeper end of the pit are seen to be steeper than in the case of the dome. Since the pit on the clinopinacoid was taken as the basis from which the negative corrosion crystal was built up, the actual form will necessarily be the same as the theoretical.

The pit on the prism as deduced in this theoretical way, will be seen to be potentially similar to that actually obtained by etching, if we remember, as in the case of that on the orthopinacoid, that the overhanging edge left at the lower part will be the starting point of vigorous solution and quickly removed.

We have, by these experiments, been able to deduce a generalization which may be stated as follows: The relationship between pits developed upon the various faces of the same crystal may be shown if a negative

crystal is formed by bringing together two pits from opposite faces. Then the pit on any face may be obtained by selecting a similar and parallel plane on the opposite side of the centre of symmetry of the crystal, and moving it in towards the centre, in a direction parallel with itself until it cuts off a small portion of the negative crystal. The cavity remaining in the cut off part will be the pit required.

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5. THE BEAKS.

(a) *The nature and classification of beaks.*

The formation of clawed or beaked projections from the bottoms of the pits was an early observed feature of the phenomena of etching. They may be obtained in the majority of crystals under favourable circumstances. Their formation is however not at all what one would expect. It has been shown by Becke,[28] that in the central, open part of the pit, currents produced in the process of etching would remove the solvent as it became saturated with the products of solution and thus expose a fresh supply of unneutralized corrosive. In the corners of the pits this would not go on so rapidly, and action would not be so vigorous. This would tend to make the production of beaks an impossibility, and so it becomes a matter of interest to devise some explanation for their existence.

The foregoing experiments show the existence of three types of beaks, two of which are heretofore undescribed. We have, in the first place, that form which extends from one corner of the pit, and which is apparently superficial, and which may be called the "crack beak" (Plate XXVII, fig. 35). In the second place we have the normal beak extending from the deepest part of the pit, and in the third the tubular beak, which may have no apparent connection with any pit, and which may extend for a considerable distance within the body of the crystal.

(b) *The crack beaks.*

The characteristics of the crack beak are described in greater detail in the case of colemanite, but examples were also observed in the etching of diopside. It appears like a crack extending in the direction of the production of the longer side of the pit through one of the acute angles. It is evident that on any crystal face parallel to the vertical axis in any crystallographic system, except the isometric, the direction of the most easy and rapid solution will be indicated by the longest side of the pit, and that inclined toward this and parallel to another side of the pit,

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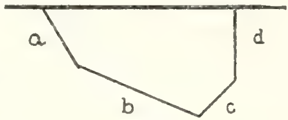
[28] Min. u. petr. Mitth., 7: 240. 1885.

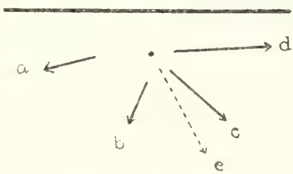
there is a direction of slowest solubility or greatest resistance. The crack beaks are then merely extensions of the longest side of the pit in the line of least resistance.

(*c*) *The normal beaks.*

The processes which result in the formation of normal beaks are, like those leading to beaks of the other types, so obscure that any attempt at discovering them is beset with many difficulties, but some of the facts observed in the foregoing experiments seem to suggest an explanation. The fundamental fact should first be noted that the beaks always spring from the deepest part of the pit. Many times pits were observed which had this deepest part developed in such a way as to warrant the conclusion that beaks were just beginning to grow. In some cases one of the side walls was seen to be steep, vertical or even overhanging. In others, the deepest part, at the base at such a steep side had become enlarged so as to form a knob-like projection. The forces acting upon a particle of the solvent in such a narrow corner, are indicated in the diagram. Of the four figure faces here indicated

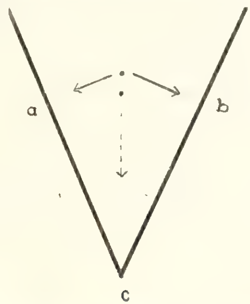


in the diagram, the longest, *b*, is the most slowly attacked and therefore has the least attraction for the particles of the solvent, while the smaller, *a*, *c*, and *d*, are those of most rapid solution and therefore of greatest attraction. In consequence each particle of the solvent is under the influence of forces which draw it toward the faces illustrated, and will move in the resultant direction *e*. The most



rapid solution, then, will take place at the point where the line of motion strikes a face of the pit. The result of such action will naturally be to accentuate the depth of the deepest part.

Any such deep corner will be the starting point of a beak, in the form at first of a somewhat tapering excavation. A particle of the solvent in a position within this, will be attracted by forces in the directions *a* and *b*, and will tend to follow their resultant in the direction *c*, and thus



increase the length of the excavation. The transition from this to a normal beak can readily be conceived.

(*d*) *The tubular beaks.*

The processes which are here described as tubular beaks, and which consist of capillary tunnels running in various directions throughout the crystal, might be supposed to be the result of the enormous development of noımal beaks. But this cannot have been their mode of origin, for the action described in the previous section could not take place in such a narrow space. Many of them indeed are apparently not connected with pits. Their growth is probably due to the ease with which corrosion can take place parallel with a cleavage plane, and which is so pronounced that such directions have been called "solution planes".

Several examples were observed in which two pits were joined by a connecting tube which evidently owed its existence to such a cause. If conditions were such that the tubes could develop along these planes the result would be a number of cavities arranged in a definite crystallographic direction. But in the most pronounced cases the tubes were not confined to any plane. Their irregularity must have been due to their deflection from their ordinary course by coming in contact with successive points of weak cohesion.

This phenomenon is of interest in view of modern theories of the origin of schillerization. For many years this has been known to be

due to the presence of numerous inclusions arranged in parallel position. They are usually of a definite crystalline form, often similar to that of the host, but sometimes they are branching or trichitic inclusions of varied outline. Now Judd has pointed out[29] that, while the inclusions have a crystalline form, they are isotropic and the form therefore cannot be their own. "I am led to the conclusion that the substances forming the various enclosures do not consist of any definite chemical compounds assuming the regular crystalline form belonging to mineral species but that they are a mixture of various oxides in a more or less hydrous condition, such as hyalite, opal, gothite and limonite, hence their isotropism, their varieties in colour and their resistance to the action of acids". In other words the inclusions are pseudomorphs.

It was also shown that while all the inclusions had one parallel pair of faces, the rest of their outlines were very frequently irregular, and closer examination revealed the fact that in these cases the inclusion did not completely fill its cavity. In view of this Judd adds: "The suggestion which seems to me to be most in accord with all the facts of the case is that those enclosures are of the nature of negative crystals which are more or less completely filled with the foreign substance, the enclosures assume the outlines of true crystals, though they do not of course exhibit their optical properties".

Goldschmidt has shown in the paper above referred to that if an etched crystal be placed in a saturated solution of the same substance the pits themselves attract the dissolved particles and in consequence immediately become filled. It follows then that such negative crystals cannot have been left in the growth of the host. Judd suggests that they may have been due to the subsequent action of etching, though he does not offer any explanation of its occurrence within the substance of the crystal and not on its surface.

Further, schillerization is to be observed only in deep-seated rocks, and Judd believes that as the silicates are known to be soluble to a certain extent in water at a great heat and under high pressure, it is to this action that we are to look for the cause both of the corrosion resulting in the production of the negative crystals and of their subsequent filling with foreign material. According to the conclusions reached in the paper above quoted, schillerization is due to a process of etching which attacks the interior of the crystal rather than its surface, and to the subsequent filling of the cavities so formed by an isotropic substance derived from the mineral itself.

The only stage in the process left unexplained is the formation of

[29] Quart. Jour. Geol. Soc., 41: 384. 1885.

the negative crystals by etching, and the experiments described in the preceding paragraphs appear to give some indications of the conditions under which this would take place in nature. In the laboratory we have a gentle corrosive—dilute hydrofluoric acid at 100°—acting for a considerable time upon a crystal, in nature we have a corrosive perhaps equally mild—water at a high temperature and pressure—acting upon a crystal for a much greater time, and the results are quite comparable. It is true that the channels and negative crystals in the natural examples may be much larger than in the artificial, a result quite in keeping with the fact, which these experiments illustrate, that slow etching tends to make possible the production of larger etch-figures. Furthermore as a link in the chain of evidence, it is interesting to remember that naturally etched crystals are occasionally met with, as, for example, that of spodumene from Alexander, N.C., described by Dana.[30]

[30] Zeitsch. für Kryst., 6: 509.

EXPLANATION OF FIGURES.

Fig. 1. Immature pit in shallow depression, Colemanite (010), 1% Acetic Acid, 100°.

Fig. 2. Two adjacent pits connected by a tube, Colemanite (010), 1% Acetic Acid, 100°.

Fig. 3. Immature pit in shallow depression, Colemanite (010), 1% Hydrochloric Acid, 100°.

Fig. 4. Pits in parallel arrangement, Colemanite (010), 2% Hydrochloric Acid, 100°.

Fig. 5. Pit on Colemanite (010), 2% Hydrochloric Acid, 100°, after second exposure.

Fig. 6. Deep pit remaining after a third exposure as above.

Fig. 7. Typical symmetrical pit, Colemanite (010), 100°, third exposure.

Fig. 8. Asymmetric pit, Colemanite (010), 4% Hydrochloric Acid, 100°.

Fig. 9. Beaked pit, Colemanite (010), 6% Hydrochloric Acid, 100°.

Fig. 10. Very immature pit, Spodumene (110), Sulphuric Acid and Fluorite, 15 minutes.

Fig. 11. Second type of pit, less immature, Spodumene, as before.

Fig. 12. Third type of pit, Spodumene (110), as before.

Fig. 13. Beaked pit, Spodumene (110), as before.

Fig. 14. Fifth type of pit showing rudimentary beak, Spodumene (110), as before.

Fig. 15. More mature pit, Spodumene (110), Sulphuric Acid and Fluoric Acid, 30 minutes.

Fig. 16. Deeper form showing a perpendicular and a curved side, Spodumene (110), as before.

Fig. 17. Four-sided pit on Spodumene (110), fused Sodium Hydrate, 2 minutes.

Fig. 18. Five-sided pit on Spodumene (110), as before.

Fig. 19. Six-sided pit on Spodumene (110), as before.

Fig. 20. Shallow five-sided pit on Spodumene (110), as before.

Fig. 21. Primitive pit, a mere shallow depression, Diopside, De Kalb, N.Y. (110), Sulphuric Acid and Fluorite, 2 minutes.

Fig. 22. Pit in second stage, Diopside (110), same corrosive, 4 minutes.

Fig. 23. Unusual asymmetric pit, Diopside, Zillerthal (110), same corrosive, 4 minutes.

Fig. 24. Typical pit, Diopside, Zillerthal (010), same corrosive, 16 minutes.

Fig. 25, 26. Asymmetrical pits, same mineral, same conditions.

Fig. 27. Pits occurring above and on either side of edge of twinning plane, Diopside, Zillerthal (010), same corrosive, 33½ minutes.

Fig. 28. Typical flat-bottomed pit, like Greim's second type, Diopside, Zillerthal (010), same corrosive, 18¾ minutes.

Fig. 29. Typical pit, Diopside, Zillerthal (100), 50% Hydrofluoric Acid, 6½ minutes.

Fig. 30. Pit on Diopside, Zillerthal (101), dilute Hydrofluoric Acid, 100°, 20 minutes.

Fig. 31. Pit on Diopside, Zillerthal (101), dilute Hydrofluoric Acid, 100°, 30 minutes.

Fig. 32. Pit on Diopside, Zillerthal (001), 50% Hydrofluoric Acid, 100°, 20 minutes.

Fig. 33. Pit on Diopside (110), fused Calcium Chloride, 15 seconds.

Fig. 34. Pit on Diopside, Zillerthal, same corrosive, 30 seconds.

Fig. 35. Colemanite etched with 10% Hydrochloric Acid, 100°, showing "crack beak".

Fig. 36. Colemanite, 2% Hydrochloric Acid, 100°, showing the position of pits on adjacent sides of a cleavage plane. The line surrounding indicates the corners of the fragment.

Fig. 37. Plaster model of diopside crystal.

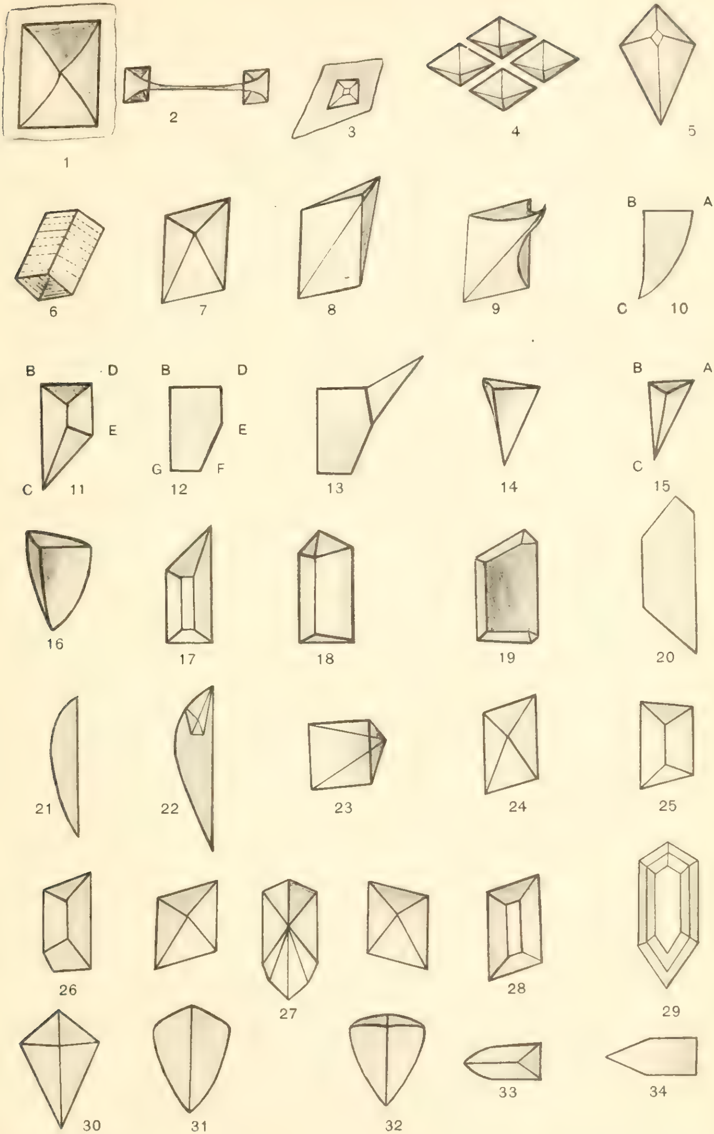
Fig. 38. Model of theoretical pit on the base.

Fig. 39. Model of theoretical pit on orthodome.

Fig. 40. Model of theoretical pit on orthopinacoid.

Fig. 41. Model of theoretical pit on prism.

Fig. 42. Model of theoretical pit on clinopinacoid.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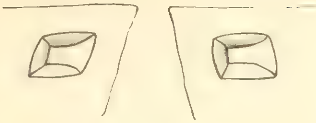

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